PHYSICAL REVIEW B VOLUME 46, NUMBER 19 15 NOVEMBER 1992-I

Band gap of strain-symmetrized, short-period Si/Ge superlattices

Janos Olajos, Jesper Engvall, and Hermann G. Grimmeiss
Department of Solid State Physics, University of Lund, Box 118, S-221 00 Lund, Sweden

Ulrich Menczigar and Gerhard Abstreiter
Walter Schottky Institut, Technische Universität München, D-8046 Garching, Federal Republic of Germany

Horst Kibbel, Erich Kasper, and Hartmut Presting
Daimler-Benz Research Center, D-7900 Ulm, Federal Republic of Germany

(Received 8 September 1992)

We report an identification and determination of the band-gap energies in a series of strain-symmetrized Si_n/Ge_n superlattices. Absorption onsets are observed that shift toward higher energies with decreasing period length in superlattices with identical Si/Ge ratio. Band-gap energies of 0.67, 0.76, and 0.88 eV for Si_6/Ge_6, Si_5/Ge_5, and Si_4/Ge_4 superlattices, respectively, are determined by a fitting procedure. Strong photoluminescence and electroluminescence are observed for the Si_5/Ge_5 superlattices. The energetic position indicates that the luminescence is related to interband transitions.

Observations of optical transitions in thin Si_n/Ge_m short-period, strained-layer superlattices[1] (SLS's) by means of electroreflectance have stimulated a great number of theoretical works even though no direct energy gap was expected in these structures. Early calculations by Gnutzmann and Clausecker in 1974 (Ref. 2) who pointed out the possibility of achieving a "quasidirect zone-folded" band gap, have been followed recently by a large number of theoretical papers predicting band offsets, band-gap energies, and optical properties.[3-16] Due to recent developments of low-temperature Si molecular-beam epitaxy (MBE), short-period superlattices have been grown with sharp interfaces on Si, Ge, and $Si_{1-x}Ge_x$ alloy buffer layers and a number of experimental investigations concerning the energy and character of the band gaps for superlattices has been reported.[17,18] The photoluminescence (PL) feature at around 0.8 eV in strain-symmetrized Si_mGe_n superlattices with a period length of 10 monolayers reported by Zachai *et al.*[18] was an experimental indication of an increased oscillator strength in a Si/Ge SLS structure. It was, however, not possible to ascribe this feature to the structurally induced "quasidirect" band gap. Later Noël *et al.*[19] and Terashima, Tajima, and Tatsumi[20] showed that similar PL features were also present in annealed, pseudomorphically grown $Si_{1-x}Ge_x$ alloys and quantum wells, i.e., in structures where no zone folding is expected. Therefore, the latter authors attributed the photoluminescence signal, tentatively, to point or line defects in the buffer layer. Their interpretation was supported by *ab initio* calculations performed by Schmid *et al.*[13,15,16] within the local-density approximation, giving band-gap energies about 200–250 meV higher than the reported luminescence.[18] The authors suggested that the luminescence may be related to misfit dislocations which are present in rather high densities. Considerable lower band-gap energies than those of Schmid *et al.* with values of about 0.65–0.9 eV have been reported by other authors[12] employing the empirical pseudopotential formalism.

In this paper we report on the identification and determination of the band gap in a series of strain-symmetrized Si_nGe_n SLS's using absorption measurements in mesa *p-i-n* structures. Furthermore, we report on electroluminescence (EL) and PL measurements in a Si_5Ge_5 superlattice, which are close in energy to the absorption onset in the SLS. The SLS structure used for this study is a series of samples (B2212–B2216, B2219) grown on a p^+ substrate by MBE at low temperatures ($300\,°C \leq T_g \leq 400\,°C$). The series consists of one Si_4Ge_4 (B2212), two Si_5Ge_5 (B2213 and B2214), and one Si_6Ge_6 (B2215) SLS structure as well as a $Si_{0.5}Ge_{0.5}$ alloy (B2216) and a Si homojunction (B2219). The two latter were used as reference samples. The SLS's were grown on a partially relaxed, 50-nm-thick $Si_{0.25}Ge_{0.75}$ alloy, corresponding to opposite strain in the consequent Si and Ge SLS layers. The thicknesses of the SLS's were chosen to be around 250 nm which amounts to 180 periods in, e.g., a 10-monolayer structure. The samples were characterized in detail with Raman, transmission electron microscopy (TEM), and x-ray diffraction. The results concerning period lengths, layer thicknesses, etc. are presented elsewhere.[21] The in-plane strain ($\varepsilon_\parallel$) in the Si layers as determined with TEM were 0.027, 0.024, 0.022, and 0.0256 for samples B2212–B2215, respectively. The actual period length deviated somewhat from the nominal. For the nominal (4:4), (5:5), and (6:6) SLS's an actual period length of (3.9:4.9) (B2212), (4.5:6.8) (B2213), (4.3:6.4) (B2214), and (5.1:7.5) B2215 were determined, respectively. The SLS's were overgrown with an *n*-type alloy and an n^+ Si layer to provide the *pn* junction and contact (Fig. 1). Two Si_5Ge_5 SLS's were grown on different buffers. The B2214 sample was grown on a 1000-nm $Si_{0.5}Ge_{0.5}$ alloy, whereas the other (B2213) was grown as the rest of the series.

The optical spectra were measured by two different methods in order to exclude systematic errors: a steady-state, short-circuit current (SC) technique with the sample illuminated by monochromatic light from a grating

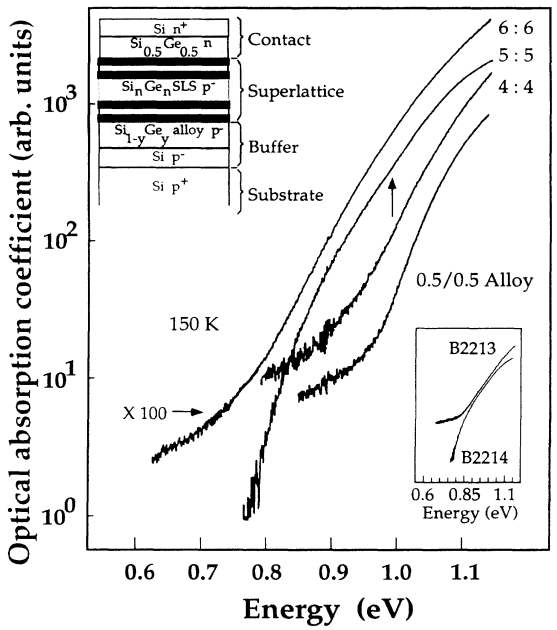

FIG. 1. Absorption spectra as measured with the short-circuit current spectroscopy for three superlattices: B2215 $=Si_6Ge_6$; *B*2214$=Si_5Ge_5$; *B*2212$=Si_4Ge_4$; and B2216 a $Si_{0.5}Ge_{0.5}$ alloy.

monochromator and another where the samples were illuminated with a broad-band, modulated beam from a Fourier-transform infrared spectrometer. Similar spectra were obtained with both methods. Since the short-circuit current is generated in the space-charge region of the n^+-p diodes,[22] this implies that the SC originates from the superlattice region. It can be shown[23] that the photoinduced SC is proportional to the absorption coefficient, α (cm^{-1}), if the absorbing layer is much thinner than α^{-1}. This is valid in our case. In Fig. 1 the absorption spectra of the various SLS samples are replotted as a function of photon energy. In the measurements, a tungsten quartz-halogen lamp, a quartz beam splitter, and a room-temperature Si filter were used. The measurement temperature was chosen as 150 K in order to obtain optimum performance of the *p-n* junctions and to maximize the band-gap signal with respect to defect-related signals but similar, though more noisy results were obtained at 77 K. Characteristic of all SLS spectra, except B2214, is a structureless, rather weak, defect-related signal at lower energies and a strong onset in the region of 0.65–0.94 eV. This onset shifts toward higher energies with decreasing SLS period length. The defect-related signal at lower energies was absent for sample B2214 which instead showed an additional, weak onset at around 0.95 eV (arrow). The onset of the strong absorption at about 0.76 eV was observed in both Si_5Ge_5 samples (B2213 and B2214) (see inset of Fig. 1) showing that this signal originates from the SLS itself and not from the buffer. The thicker buffer of B2214 apparently improved the quality of the SLS (lower defect density), but also gave rise to detectable band-gap absorbance in the alloy buffer layer at somewhat higher energies. These observations clearly demonstrate that the superlattice band gap is *smaller* than the band gap of an alloy with the same Si/Ge composition.

The band-gap energy E_g is readily determined from the SC measurements by fitting the expression for the absorption coefficient, $\alpha \sim (h\nu - E_g)^2$ to the experimental data. The inset of Fig. 2 shows the square root of the absorption versus photon energy of sample B2214 (Si_5Ge_5) and sample B2215 (Si_6Ge_6). The nearly straight lines suggest that α is proportional to $(h\nu - E_g)^2$ and this expression is therefore used to determine E_g. For bulk, three-dimensional semiconductors, a parbolic band structure and a constant optical matrix element M_{if} are used when calculating the energy dependence of the absorption coefficient in the vicinity of the band gap.[24] Neither of these assumptions is valid in a superlattice.[10] Accordingly, no simple analytical expression can be employed when considering if indirect or quasidirect transitions are observed. Although no detailed theoretical analysis of the spectral dependence of α in the vicinity of the fundamental band gap of such superlattices is available, there are some calculations by Churchill *et al.*[25] and Gell.[26] Their calculated spectra indicate that our experimentally determined expression can be used. The fitting procedure which has been applied for the determination of E_g is demonstrated in Fig. 2 for two typical samples, B2215 and B2214. The 6:6 superlattice which is grown on the thin buffer shows one major onset and a tail towards lower energies. The weaker signal at lower energies can be fitted with a defect activation energy of 0.2–0.4 eV. The exact determination of this energy is not essential for the purpose of this paper. The signal at higher energy is best fitted with a single onset which leads to a band-gap energy of 0.67 eV (±0.01 eV). No additional onsets at higher energies are observed in this sample. Therefore,

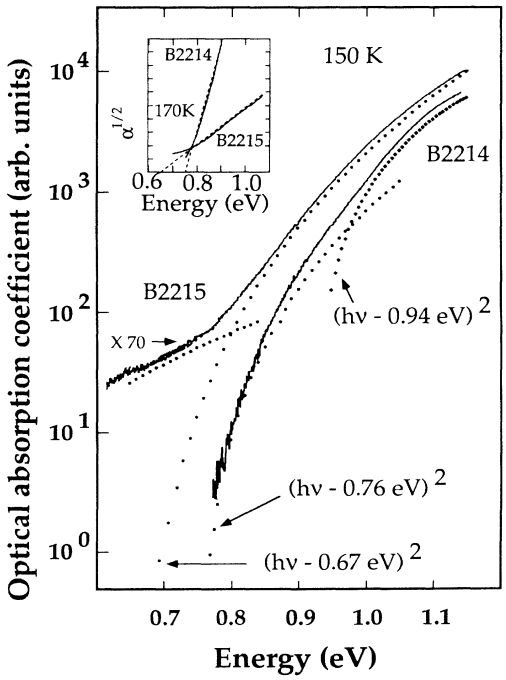

FIG. 2. Fitting procedure for two typical samples B2215 $=Si_6Ge_6$ and B2214$=Si_5Ge_5$. The additional onset in the spectrum of B2214 originates from the thick alloy buffer layer.

we believe that the onset at 0.67 eV is due to band-to-band transitions and reflect the fundamental energy gap of the Si_6Ge_6 superlattice. As mentioned earlier, the spectrum of sample B2214 showed no defect-related absorption. The total absorption curve is readily described by two absorption processes with threshold energies of 0.76 and 0.94 eV. We believe that the 0.76-eV onset is due to the band gap of the Si_5Ge_5 SLS and that the signal starting at 0.94 eV originates from the thick buffer layer. Indeed, a similar absorption onset at 0.94 eV is observed for the $Si_{0.5}Ge_{0.5}$ alloy reference sample (Fig. 1).

We have modeled the energy gaps of the superlattice structures using the Kronig-Penney (KP) approximation[27] together with band offsets given by Van de Walle and Martin.[7] The bulk effective masses in the appropriate k direction were used for the Si and Ge layers, respectively. These results, together with the experimental data and the values presented in other theoretical papers, are shown in Fig. 3. When comparing the theoretical data of Turton and Jaros[12] and Schmid *et al.*[13] to the data presented in this paper, one must take into consideration the fact that experimental strains are larger than the exact strain symmetrization assumed in theory. While absolute values of band-structure calculations have to be treated with care, the relative energy difference of samples with different period lengths should nevertheless give valuable information. Figure 3 shows that the overall trend in the experimental energy gaps is in good agreement with empirical pseudopotential calculations[12] of strain-symmetrized Si_nGe_n superlattices. Also the KP model leads to similar trends. The band-gap energy calculated by Schmid *et al.*[13,15,16] for the Si_5Ge_5 SLS is, however, considerably higher.

The samples were also studied with respect to PL and EL. PL spectra were excited with an Ar^+-ion laser using an excitation power density of 50 W/cm^2 and $\lambda_{laser}=457$ nm. The EL spectrum was obtained with an injected electrical power of 20 mW. The temperature in the EL experiment is uncertain since the diode is warmed up by the injected power. The luminescence spectra are not corrected for the spectral dependence of the optical setup. The low-energy cutoff of the liquid-N_2-cooled Ge detector is about 0.7 eV. In Fig. 4, PL spectra for sample B2216 (d), B2213 (c), and B2214 (b) are compared with the EL spectrum of B2214 (a). The broad and weak PL signals of sample B2216 observed below the band gap of the alloy can be attributed to defect-related transitions.[28] The PL spectrum of sample B2213 (c) is qualitatively different compared to the PL spectrum of sample B2216 (d). Only one PL line is observed which appears at lower energies compared to the defect-related PL signals. The PL signal observed for sample B2214 is detected at almost the same energetic position; however, the PL intensity is about an order of magnitude higher which gives further evidence for the improved quality of the sample. A dislocation density of one order of magnitude less than in the 10-monolyer samples used in the work of Zachai *et al.*[18] was determined in sample B2214.[29] Only in the 10-monolayer-period SLS was this PL feature observed. This is most likely due to the fact that no SLS with shorter and longer period lengths were available which were grown on the thick, high-quality buffer layer.

The strong PL signals originate in the superlattice region since the signal disappears if the superlattice is carefully removed by wet chemical etching.[21] A further confirmation of the origin of the PL is obtained by the EL results. Carriers injected into the diode structure recombine in the depletion region since the current through the diode is a recombination current as determined from the ideality factor of the I-V characteristics, this value varying between 1.7 and 2.2 in the temperature interval of 300 to 77 K. The width of the depletion region at $U=0$ V is about 200 nm, i.e., smaller than the region of the superlattice. EL spectra should therefore be similar to PL spectra due to the fact that both spectra originate from the superlattice itself. This is indeed true for the investigated sample as shown in Fig. 4. For low injection power, line shapes and energy positions of EL and PL signals are very similar. Furthermore, the PL peak is in good agreement with the band-gap energy of

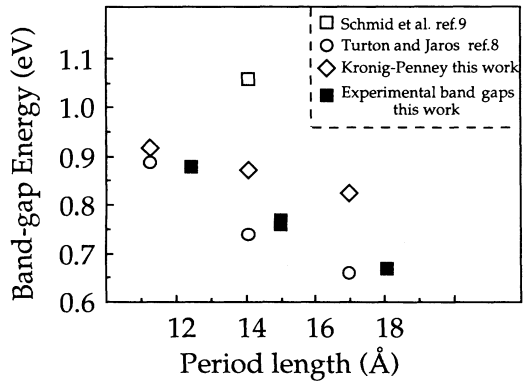

FIG. 3. Experimentally determined band-gap energies compared with some theoretical values.

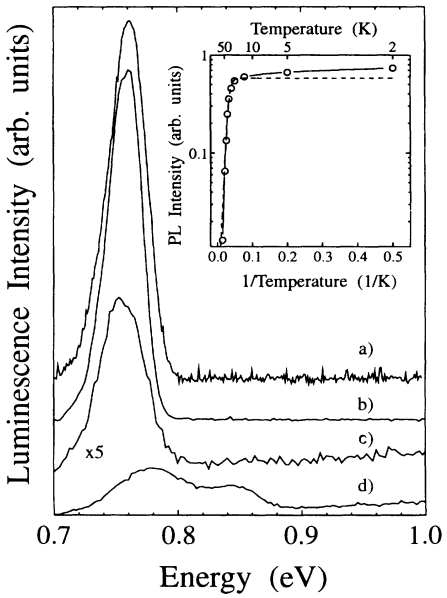

FIG. 4. Photoluminescence spectra of samples B2216 (d), B2213 (c), and B2214 (b) and electroluminescence spectrum of B2214 (a). The inset shows the temperature dependence of the PL peak of sample B2214.

0.76 eV obtained from absorption measurements at 150 K. Using a linear interpolation of the band-gap temperature dependence between those of Si and Ge, an energy difference of 20 meV between the onset of the absorption and the PL signal is observed. This energy difference may be explained by the excitonic binding energy plus a Stokes shift, resulting in values of 9 and 6 meV. The temperature dependence of the PL intensity is shown in the inset of Fig. 4. The PL intensity is decreasing continuously with increasing temperature and can be followed up to 60 K connected with a few meV shift of the peak energy to lower energies. The fitted temperature dependence is plotted as a dashed line. The activation energy E_a as determined with this fit is 15 meV. On the high-energy side of the PL line, a broadening is observed with increasing temperature which suggests that the SLS PL is due to an excitonic no-phonon transition. The relatively large full width at half maximum (FWHM) in our samples compared to PL spectra in pseudomorphic multiquantum wells (MQW) are due to a slight nonuniformity in the structures concerning strain and period thickness. Luminescence studies of Terashima, Tajima, and Tatsumi[20] and Noël *et al.*[19] on $Si_{1-x}Ge_x$ MQW grown with MBE at low temperatures revealed PL signals which they attributed to strain localized excitons. The PL signals in the paper of Noël *et al.*[19] are observed about 100 meV below the expected band gap. Spitzer *et al.*,[30] however, observed excitonic band-gap luminescence in MBE-grown pseudomorphic $Si_{1-x}Ge_x$ alloys even at growth temperatures as low as 325 °C. In addition to this band-gap luminescence, defect-related PL signals with a FWHM of 100 meV could be observed at about 150 meV below the measured band gap. As our SLS's are grown in the same MBE chamber under similar conditions, growth defects similar to those observed by Spitzer *et al.*[30] are expected also in the samples investigated in this work. From the optical measurements presented in this paper we have good reasons to believe that the defect activation energies in our strain-symmetrized structures are of the order of 0.2–0.5 eV in agreement with earlier defect studies on strain-symmetrized samples.[31] The agreement of the transition energies obtained by PL and absorption, and the fact that the absorption signal originates from the depletion layer, i.e., the superlattice itself, suggests that also in PL interband transitions are observed. These interband transitions are due to carriers localized in the superlattice region. According to the simple KP calculation used to determine band-gap energies, we obtain a band lineup where the minibands resulting in the valence-band maximum and conduction-band minimum are localized in the strain-symmetrized superlattice region.

In conclusion, we have determined the band-gap energies of a series of strain-symmetrized Si_nGe_n SLS's. This was done by absorption measurements in mesa *p-i-n* diode structures. The experimental values were compared to various theoretical data and a good coincidence was found in the trend of the band-gap energies as a function of period length with calculations using the empirical pseudopotential method. Strong PL and EL signals were observed at the band-gap energy in the Si_5Ge_5 SLS and thus it was possible to attribute these luminescence signals to interband transitions.

This work has been supported by a grant under the ESPRIT basic research European programme, Contract No. P-3174. The authors acknowledge valuable discussions with M. Jaros.

[1]T. P. Pearsall *et al.*, Phys. Rev. Lett. **58**, 729 (1987).
[2]U. Gnutzmann and K. Clausecker, Appl. Phys. **3**, 9 (1974).
[3]S. Froyen, D. M. Wood, and A. Zunger, Phys. Rev. B **36**, 4547 (1987); **37**, 6893 (1988).
[4]M. S. Hybertsen and S. Schlüter, Phys. Rev. B **36**, 9683 (1987); M. S. Hybertsen *et al.*, *ibid.* **37**, 10 195 (1988).
[5]L. Brey and C. Tejedor, Phys. Rev. Lett. **59**, 1022 (1987).
[6]M. A. Gell, Phys. Rev. B **38**, 7535 (1988).
[7]C. G. Van de Walle and Richard M. Martin, Phys. Rev. B **34**, 5621 (1986).
[8]I. Morrison *et al.*, Phys. Rev. B **35**, 9693 (1987).
[9]K. B. Wong *et al.*, Phys. Rev. Lett. **60**, 2221 (1988).
[10]R. J. Turton *et al.*, Phys. Rev. B **38**, 8397 (1988).
[11]M. Jaros *et al.*, J. Electron. Mater. **19**, 35 (1990).
[12]R. J. Turton and M. Jaros, Mat. Sci. Eng. B **7**, 37 (1990).
[13]U. Schmid, N. E. Christensen, M. Cardona, and M. Alouani, in *Proceedings of the 20th International Conference on the Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 865.
[14]U. Schmid *et al.*, Phys. Rev. B **41**, 5919 (1990).
[15]U. Schmid *et al.*, Phys. Rev. Lett. **65**, 1933 (1990).
[16]U. Schmid *et al.*, Phys. Rev. B **43**, 14 597 (1991).
[17]T. Pearsall *et al.*, Phys. Rev. Lett. **63**, 2104 (1989).
[18]R. Zachai *et al.*, Phys. Rev. Lett. **64**, 1055 (1990).
[19]J.-P. Noël *et al.*, Appl. Phys. Lett. **57**, 1037 (1990).
[20]Koichi Terashima *et al.*, Appl. Phys. Lett. **57**, 1925 (1990).
[21]H. Presting, U. Menczigar, G. Abstreiter, H. Kibbel, and E. Kasper, MRS Conf. Proc. No. 256 (Materials Research Society, Pittsburgh, 1992), pp. 83–88.
[22]S. Braun and H. G. Grimmeiss, J. Appl. Phys. **44**, 2789 (1973).
[23]D. V. Lang *et al.*, Appl. Phys. Lett. **47**, 1333 (1985).
[24]J. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).
[25]A. C. Churchill *et al.*, Semiconduct. Sci. Technol. **6**, 18 (1991).
[26]M. A. Gell, Semiconduct. Sci. Technol. **5**, 449 (1991).
[27]G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Editions de Physique, Paris, 1988).
[28]J. Weber and M. I. Alonso, in *Defect Control in Semiconductors,* edited by K. Sumino (Elsevier North-Holland, Amsterdam, 1990) p. 1453.
[29]W. Jäger, D. Stenkramp, P. Ehrhart, K. Leifer, W. Sybertz, H. Kibbel, H. Presting, and E. Kasper (unpublished).
[30]J. Spitzer, K. Thonke, R. Sauer, H. Kibbel, H. J. Herzog, and E. Kasper (unpublished).
[31]H. G. Grimmeiss *et al.*, Phys. Rev. B **45**, 1236 (1992).

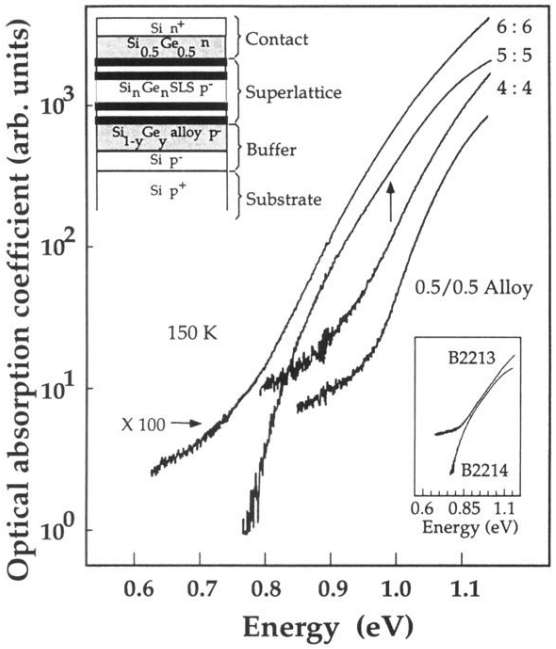

FIG. 1. Absorption spectra as measured with the short-circuit current spectroscopy for three superlattices: B2215 $=Si_6Ge_6$; *B*2214$=Si_5Ge_5$; *B*2212$=Si_4Ge_4$; and B2216 a $Si_{0.5}Ge_{0.5}$ alloy.